

New ideas in glass transitions

Giorgio Parisi

Dipartimento di Fisica, Università *La Sapienza*

INFN Sezione di Roma I

Piazzale Aldo Moro, Roma 00187

February 7, 2008

Abstract

In this talk I will review some of the recent applications of the replica theory to glasses. I will firstly describe the basic assumptions and I will show that they can be considered as a precise reformulations of old ideas. The relation of this approach with the mode-coupling theory will be shortly discussed.

I will present numerical simulations for binary mixtures. The results of these simulations point toward the correctness of the replica approach to glasses. I will describe the results of off-equilibrium simulations for large systems, in which the aging dynamics is studied.

In this talk I will review some of the theoretical progresses that have been done in our understanding of glasses. They have been done mainly by comparing the results obtained for soluble models of generalized spin glasses with structural glasses assuming that the phase space of the two models are similar.

In the nutshell many of the ideas I am going to present are not new: they are already in the original papers of Gibbs and Di Marzio. However the comparison of glasses and generalized spin glasses, introduced in ref. [1] allow us to put these ideas in a sharper form and to test them in numerical (and eventually real) experiments. In this talk I will not discuss the theoretical basis under which this scenario has been derived (i.e. the mathematical tool needed to derive the results stated for the generalized spin glasses) but I will concentrate the attention of the physical picture.

The basic ideas are quite simple [2, 3, 4, 5, 6, 7, 8]. Let us consider a system of N particles and let us assume that we can introduce a free energy functional $F[\rho]$ which depends on the density $\rho(x)$ and on the temperature. We suppose that at sufficiently low temperature this functional has many minima (i.e. the number of minima goes to infinity with the number (N) of particles). Exactly at zero temperature these minima coincide with the minima of the potential energy as function of the coordinates of the particles. Let us label then by an index α . To each of them we can associate a free energy F_α and a free energy density $f_\alpha = F_\alpha/N$.

In this low temperature region we suppose that the total free energy of the system can be well approximated by the sum of the contributions to the free energy of each particular minimum:

$$Z \equiv \exp(-\beta N f_S) = \sum_{\alpha} \exp(-\beta N f_{\alpha}). \quad (1)$$

When the number of minima is very high, it is convenient to introduce the function $\mathcal{N}(f, T, N)$ which is the density of minima whose free energy is equal to f . With this notation we can write the previous formula as

$$Z = \int df \exp(-\beta N f) \mathcal{N}(f, T, N). \quad (2)$$

In the region where \mathcal{N} is exponentially large we can write

$$\mathcal{N}(f, T, N) \approx \exp(N \Sigma(f, T)), \quad (3)$$

where the function Σ is called the complexity or the configurational entropy (it is the contribution to the entropy coming from the existence of an exponentially large number of locally stable configurations).

The relation (3) is valid in the region $f_m(T) < f < f_M(T)$. The minimum possible value of the free energy is given by $f_m(T)$. Outside this region we have that $\mathcal{N}(f, T) = 0$. In all cases known $\Sigma(f_m(T), T) = 0$, and the function Σ is continuous at f_m .

For large values of N we can write

$$\exp(-N \beta f_S) \approx \int_{f_m}^{f_M} df \exp(-N(\beta f - \Sigma(f, T))). \quad (4)$$

We can thus use the saddle point method and approximate the integral with the integrand evaluated at its maximum. We find that

$$\beta f_S = \min_f \Phi(f) \equiv \beta f^* - \Sigma(f^*, T), \quad (5)$$

where

$$\Phi(f) \equiv \beta f - \Sigma(f, T). \quad (6)$$

(This formula is quite similar to the well known homologous formula for the free energy ,i.e. $\beta f = \min_E(\beta E - S(E))$, where $S(E)$ is the entropy density as function of the energy density.)

If we call f^* the value of f which minimize $\Phi(f)$. we have two possibilities:

- The minimum is inside the interval and it can be found as solution of the equation $\beta = \partial \Sigma / \partial f$. In this case we have

$$\beta \Phi = \beta f^* - \Sigma^*, \quad \Sigma^* = \Sigma(f^*, T). \quad (7)$$

The system may stay in one of the many possible minima. The number of minima at which is convenient for the system to stay is $\exp(N \Sigma^*)$. The entropy of the system is thus the sum of the entropy of a typical minimum and of Σ^* , which is the contribution to the entropy coming from the exponential large number of microscopical configurations.

- The minimum is at the extreme value of the range of variability of f . We have that $f^* = f_m$ and $\Phi = f_m$. In this case the contribution of the complexity to the free energy is zero. The different states who contribute to the free energy have a difference in free energy density which is of order N^{-1} (a difference in total free energy of order 1). Sometimes we indicate the fact that the free energy is dominated by a few different minima by saying that the replica symmetry is spontaneously broken [9, 10].

Form this point of view the behaviour of the system will crucially depend on the free energy landscape [11], i.d. the function $\Sigma(f, T)$, the distance among the minima, the height of the barriers among them... Although our final task should be to compute the properties of the free energy landscape from the microscopic form of the Hamiltonian, we can tentatively assume that the landscape of fragile glasses is similar to that of some soluble long range models in presence of quenched disorder [1, 11].

I cannot discuss here in details the rationale for this hypothesis; it is also clear that it cannot be exact and some differences should be present among the predictions of the mean field approximation and the real world. Here I will present the scenario coming from mean field, stressing some of the predictions that should have a wider range of validity and comparing them with numerical simulations for fragile glasses.

We can distinguish a few temperature regions.

- For $T > T_f$ the only minimum of the free energy functional is given by a constant density. The system is obviously in the fluid phase.
- For $T_f > T > T_D$ there is an exponentially large number of minima with a non-constant density $\rho(x)$ [5, 12]. There are values of the free energy density such that the complexity Σ is different from zero, however the contribution coming from these minima is higher than the one coming from the liquid solution with constant $\rho(x)$.
- The most interesting situation happens in the region where $T_D > T > T_K$. In this region the free energy is still given by the fluid solution with constant ρ and at the same time the free energy is also given by the sum over the non trivial minima [7, 8].

Although the thermodynamics is still given by the usual expressions of the liquid phase and final free energy is analytic at T_D , below this temperature the liquid phase correspond to a system which at each given moment may stay in one of the exponentially large number of minima. It is extremely surprising that the free energy of the liquid can be written in this region as the sum of the contribution of the minima, according to formula (4).

The time to jump from one minimum to an other minimum is quite large: it is an activated process which is controlled by the height of the barriers which separate the different minima. The correlation time will become very large below T_D and for this region T_D is called the dynamical transition point. The correlation time (which should be proportional to the viscosity) should diverge at T_K . The precise form of this divergence is not well understood. It is natural to suppose that we should get divergence of the form $\exp(A/(T - T_K)^\nu)$ for an appropriate value of ν , whose reliable analytic computation is lacking [1, 16].

The equilibrium complexity is different from zero (and it is a number of order 1) when the temperature is equal to T_D and it decreases when the temperature decreases and it vanishes linearly at $T = T_K$. At this temperature (the so called Kauzmann temperature) the entropy of a single minimum becomes the total entropy and the contribution of the complexity to the total entropy vanishes.

- In the region where $T < T_K$ the free energy is dominated by the contribution of a few minima of the free energy having the lowest possible value. Here the free energy is no more the analytic continuation of the free energy in the fluid phase. A phase transition is present at T_K and the specific heat is discontinuous here.

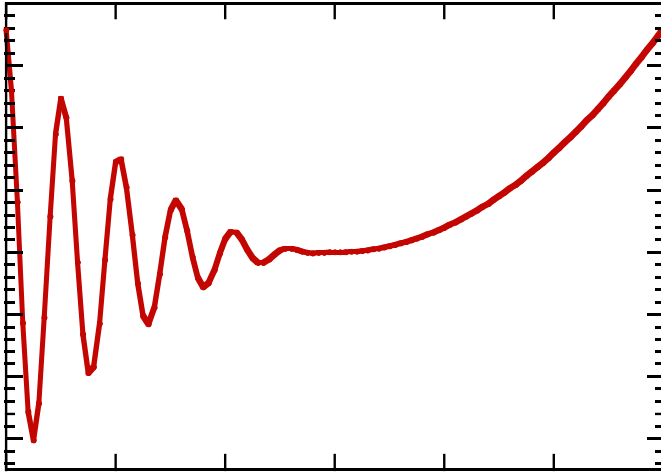


Figure 1: The qualitative dependence of the free energy as function of the configuration space in the region relevant for the dynamical transition, i.e. for $T < T_D$.

The free energy landscape is quit usual; we can try to present the following pictorial interpretation, which is a rough simplification [13]. At temperature higher than T_D the system stays in a region of phase space which is quite flat and corresponds to a minimum of the total free energy. On the contrary below T_D the phase space is similar to the one shown pictorially in fig. 1. The region of maxima and minima is separated by the region without barriers by a large nearly flat region. The minima in the region at the left are still present also when $T_f > T > T_D$, but they do not correspond to a global minimum.

At temperatures higher than T_D the system at thermal equilibrium states in the right region. When the temperature reaches T_D the system arrives in the flat region. Here the potential is flat and this causes a more or less conventional Van Hove critical slowing down which is well described by the well known mode coupling theory [14] (which is exact in the mean field approximation). The mode coupling theory describes the critical slowing down which happens near T_D [15].

In the mean field approximation the height of the barriers separating the different minima is infinite and the temperature T_D is sharply defined as the point where the correlation time diverges. In the real world activated processes (which are neglected in the mean field approximation and consequently in the mode coupling theory) have the effect of producing a finite (but large) correlation time also at T_D . The precise meaning of the dynamical temperature beyond mean field approximation is discussed in details in [3].

When the temperature is smaller than T_D we must be more precise in describing the dynamics of the system. Let us start from a very large system (of N particles) at high temperature and let us gradually cool it. We find that it should go to equilibrium in the region with many minima. However coming from high free energy (from the right) it cannot enter in the region where there are many maxima and minima if we wait a finite amount of time (the time to cross the barriers diverges as $\exp(AN)$). If we do not wait an exponentially large amount of time the system remains confined in the flat region. In this case [2] the so called dynamical energy,

$$E_D = \lim_{t \rightarrow \infty} \lim_{N \rightarrow \infty} E(t, N), \quad (8)$$

is higher than the equilibrium free energy. The situation is described in fig. 2.

Below T_D the system is trapped in metastable states when cooled. The time needed to escape from these states diverges when N goes to infinity in the mean field approach where activated processes are forbidden. Of course the difference of the static and dynamic energy is

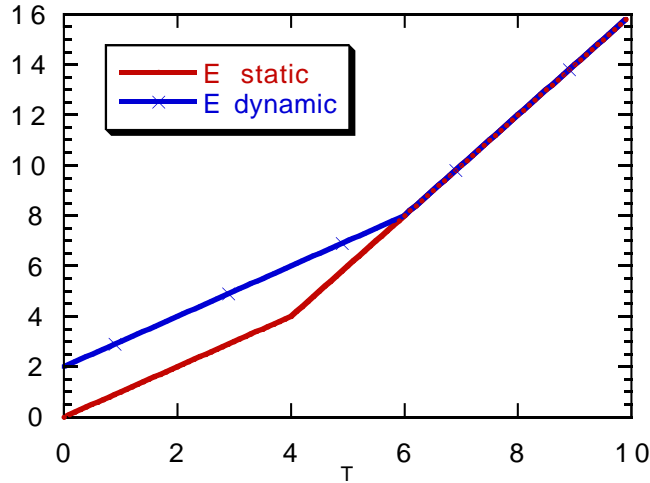


Figure 2: The qualitative behaviour of the equilibrium and of the dynamical energy as function of the temperature.

an artifact of the mean field approximation if we take literally the limit $t \rightarrow \infty$ in the previous equation because as matter of fact there are no metastable states with strictly infinite mean life. However it correctly describe the situation on laboratory times, where metastable states are observed.

In real systems, beyond the mean field approximation, the height of the barriers is finite also below T_D and the mean life of the metastable states is finite, albeit very large. Some mechanisms have been described who imply a divergence of the correlation time in real systems at the Kauzmann temperature [1, 3, 16]. The conventional glass temperature, i.e. the temperature at which the microscopic correlation time becomes macroscopic (e.g. of order of the minute) is between the two temperatures (i.e. $T_D > T_G > T_K$).

It should be clear that in this framework the dynamical temperature T_D is not so well defined and it correspond to a crossover region below it the dynamics is dominated by activated processes [3].

In the mean field approximation there are very interesting phenomena that happen below T_D when the system is cooled from the high temperature phase. These phenomena are related to the fact that the system does not really go to an equilibrium configuration but wanders in the phase space never reaching equilibrium. The phenomena are the following:

- The energy approaches equilibrium slowly when the system is cooled from an high energy configuration. In other words for large times we have

$$E(t, T) = E_D(T) + B(T)t^{-\lambda(T)}, \quad (9)$$

where the exponent $\lambda(T)$ does not vanish linearly at zero temperature as it should happens for an activated process.

- Aging is present, i.e. the correlation functions and the response functions in the region of large time do depend on the story of the system [17, 18, 19].
- In the region where aging is present the hypothesis at the basis of the fluctuation dissipation theorem are no more valid. New generalized relations are satisfied [20, 21], which replace the fluctuation dissipation theorem.
- In the region where the diffusion constant is zero, a new phenomenon, logarithmic diffusion, is present.

All these phenomena are well known also in the case of spinodal decomposition but have a more general validity.

Here I will illustrate this phenomena in the case of a monatomic fluid (I will consider the case of a binary mixture in order to avoid crystallization). The particle interacts with a soft x^{-12} potential. Half of the particles are of type A , half of type B and the interaction among the particles is given by the Hamiltonian:

$$H = \sum_{i < k} \left(\frac{(\sigma(i) + \sigma(k))}{|\mathbf{x}_i - \mathbf{x}_k|} \right)^{12}, \quad (10)$$

where the radius (σ) depends on the type of particles.

The model is well studied in the past [22, 23, 24, 25, 27]. It is known that the choice $\sigma_B/\sigma_A = 1.2$ strongly inhibits crystallisation and the system goes into a glassy phase when it is cooled. Using the same conventions of the previous investigators we consider particles of average radius 1, i.e. $(\sigma_A^3 + 2(\sigma_A + \sigma_B)^3 + \sigma_B^3)/4 = 1$. The system goes into the glass phase at $\Gamma \approx 1.45$, where we follow the standard notation: $\Gamma \equiv \beta^{1/4}$.

For reason of space I will concentrate on the properties of diffusion [26]. Let me firstly discuss the equilibrium situation and later I will discuss the non-equilibrium case.

A typical quantity that can be studied in a glass is the diffusion. We can define the average distance squared done by a particle in time t as

$$\Delta(t) = \langle (x_i(t) - x_i(0))^2 \rangle \quad (11)$$

where the label i may take values from 1 to N . The diffusion constant D is defined as

$$\Delta(t) \approx Dt \quad (12)$$

for large t .

In the following we will assume (and it is a rather good approximation) that in the glass phase $\Delta(t)$ goes to a constant (Δ^*) at large t , so that the diffusion constant D is zero.

We can also introduce the response to an external force. Let us consider the following time dependent Hamiltonian

$$H = H_0 + \epsilon(t)F \cdot x_i, \quad (13)$$

where H_0 is the original unperturbed Hamiltonian and F is a vector of length d , where d is the dimension of the space (usually 3). Both here and in eq. (11) the value of index i (i.e the particle we have chosen) is arbitrary and the result does not depend on i .

We consider the case where

$$\epsilon(t) = 0 \quad \text{for } t < 0, \quad \epsilon(t) = \epsilon \quad \text{for } t > 0, \quad (14)$$

ϵ being a small number. The response function is defined as

$$\langle F \cdot x_i(t) \rangle = \epsilon R(t) + \langle F \cdot x_i(t) \rangle|_{\epsilon=0}. \quad (15)$$

The usual fluctuation dissipation theorem tell us that

$$\beta \Delta(t) = R(t), \quad (16)$$

In the large t limit we obtain the celebrated Einstein relation among diffusion and viscosity.

Let us consider an off-equilibrium situation. Here the results depend on the history of the system. We a very simple history. The system is in the liquid phase for $t < 0$, at $t = 0$ it is

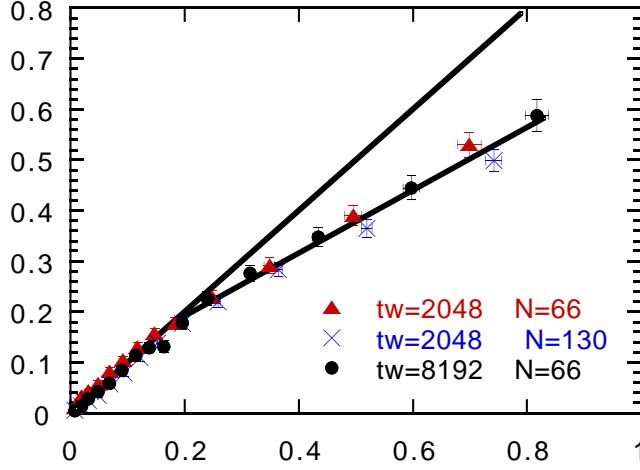


Figure 3: R versus $\beta\Delta$ at $\Gamma = 1.6$ for $t_w = 8192$ and $t_w = 2048$ at $N = 66$ and for $t_w = 2048$ at $N = 130$. The two straight lines have slope 1 and .62 respectively.

cooled very fast at the final temperature in the glassy phase. Here time translational invariance is no more present. We generalize the previous definitions introducing two times quantities:

$$\Delta(t, t_w) = \langle (x_i(t + t_w) - x_i(t_w))^2 \rangle. \quad (17)$$

The response function is defined by

$$\epsilon R(t, t_w) = \langle x_i(t + t_w) \cdot F \rangle - \langle F \cdot x_i(t + t_w) \rangle \Big|_{\epsilon=0} \quad (18)$$

where the statistical expectation values are computed with the time dependent Hamiltonian (13), where $\epsilon(t)$ given by

$$\epsilon(t) = 0 \quad \text{for } t < t_w, \quad \epsilon(t) = \epsilon \quad \text{for } t > t_w \quad (19)$$

We obviously have that

$$\lim_{t_w \rightarrow \infty} \Delta(t, t_w) = \Delta(t) \quad (20)$$

and in this way we recover the equilibrium limit.

The equilibrium limit is relevant when $t_w \gg t$. The aging regime is present when both t and t_w are both large. In the simpler case (i.e. naive aging) the interesting behaviour happens when $t = O(t_w)$ (i.e. the ratio t/t_w is finite) and t_w is large. In this regime we find that

$$\Delta(t, t_w) \approx \Delta\left(\frac{t}{t_w}\right). \quad (21)$$

In other words if we measure something on a time scale t comparable to t_w , we always see a non-equilibrium behaviour.

The generalized fluctuation dissipation theorem tells us that, if we plot at a given t_w Δ versus R , the plot has a limit when t_w goes to infinity (as an effect of aging) and we can define a function $X(\Delta)$ [2] as

$$\frac{\partial R}{\partial \Delta} = \beta X(\Delta). \quad (22)$$

The function X can be constructed for any pairs of observable and its value should not depend on the observables. More precisely, if we take two other quantities satisfying the

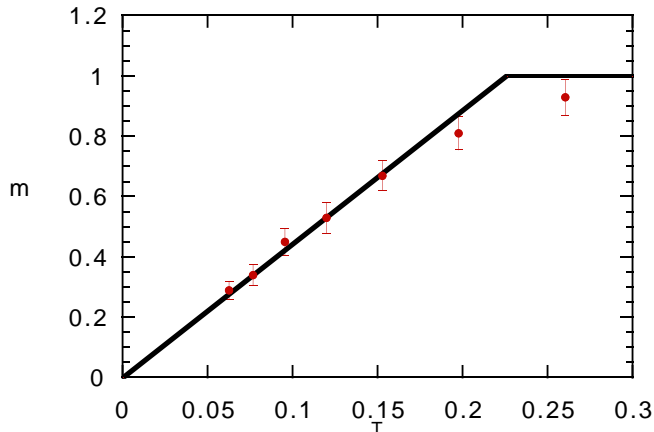


Figure 4: The quantity $m \equiv \partial R / \partial \beta \Delta$ as $t_w = 2048$ as function of the temperature. The straight line is the prediction of the approximation $m(T) = T/T_c$.

fluctuation dissipation theorem, we should have that at equal values of s the function X takes the same value of $X(\Delta)$. The fluctuation dissipation theorem is violated in the same way for all the observables at the same time.

It has been conjectured that this dynamically defined function X is related to an similar function which can be defined by measurements done only at equilibrium [2]. A precise presentation of this conjecture would take too much time. A numerical verification of its correctness in short range spin glasses can be found in [21].

The simplest non trivial form of the function $X(\Delta)$ is (in analogy to what happens in generalized spin glasses)

$$\begin{aligned} X(\Delta) &= 1 & \text{for } \Delta < \Delta^* \\ X(\Delta) &= m(T) & \text{for } \Delta > \Delta^* \end{aligned} \quad (23)$$

where $m(T)$ is approximately a linear function of the temperature taking the value one at $T = T_D$.

In other words if we plot the response R as function of $\beta \Delta$ we should find piece-linear graph with slope 1 for at small Δ and slope m for large Δ . The result of numerical simulations in the glassy phase are shown in fig. 3 (for details see ref. [26]).

Naive aging would imply that in the large time region (both times large) $\Delta(t, t_w)$ is a function of only the ration t/t_w . If we do some reasonable assumption naive aging implies that $\Delta(t, t_w)$ behaves as $A \ln(t/t_w) + B$ when t is large [28].

This phenomenon is well known in Ising spin systems. It amount to say that if we cool at zero temperature a spin system starting from an high energy configuration, the average number of times a spin is reversed increases as the logarithm of the time. This off-equilibrium logarithmic diffusion seems to be present in glasses. For example numerical simulations of a binary mixture are very well in agreement with this prediction as can be seen in fig. 5.

The results of simulations are in very good agreement with the theoretical expectations based on our knowledge extracted from the mean field theory for generalized spin glass models. The approximation $m(T) = T/T_D$ seems to work with an embarrassing precision. We can conclude that the ideas developed for generalized spin glasses have a much wider range of application than the models from which they have been extracted. It likely that they reflect quite general properties of the phase space and therefore they can be applied in cases which are very different from the original ones. In a recent work [3] some thermodynamic predictions have been obtained for the behaviour of glassy systems, like the present ones, under the assumption

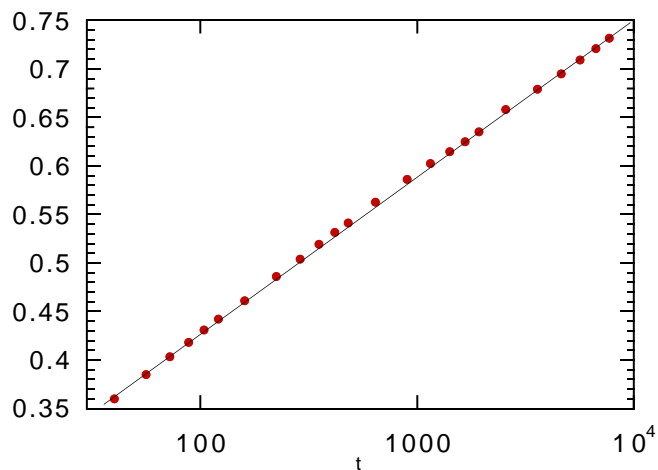


Figure 5: The average distance squared from the initial configuration (i.e. $\Delta(t, 1)$) as function of the time in a logarithmic scale for $\Gamma = 1.6$.

that they obey the laws derived for generalized spin glasses. The present work confirms that assumption.

The most urgent theoretical task would be now to develop an analytic theory for glasses in the low temperature region from which one could compute the function $m(T)$. This goal should not be out of reach: a first step in this direction can be found in [29].

References

- [1] T.R. Kirkpatrick and D. Thirumalai, Phys. Rev. Lett. **58**, 2091 (1987); T.R. Kirkpatrick and D. Thirumalai, Phys. Rev. **B36**, 5388 (1987); T.R. Kirkpatrick, D. Thirumalai and P.G. Wolynes, Phys. Rev. **A40**, 1045 (1989).
- [2] L. F. Cugliandolo and J.Kurchan, Phys. Rev. Lett. **71**, 1 (1993).
- [3] S.Franz and G. Parisi, Phys. Rev. Letters (in press) and *Effective potential in glassy systems: theory and simulations*, cond-mat/9711215.
- [4] For a review see also G. Parisi, *Proceedings of the ACS meeting*, Orlando (1996), cond-mat/9701068, *Lecture given at the Sitges conference, June 1996* cond-mat/9701034 and *Lectures given at the Varenna summer school 1996*, cond-mat/9705312.
- [5] J. Kurchan, G. Parisi, and M. A. Virasoro, J. Phys. I France **3**, 1819 (1993).
- [6] A. Crisanti and H.-J. Sommers, J. Phys. I (France) **5**, 805 (1995).
- [7] S. Franz, G. Parisi, J. Physique I **5** (1995) 1401.
- [8] R. Monasson, Phys. Rev. Lett. **75** (1995) 2847.
- [9] M. Mézard, G. Parisi and M.A. Virasoro, *Spin glass theory and beyond*, World Scientific (Singapore 1987).
- [10] G. Parisi, *Field Theory, Disorder and Simulations*, World Scientific, (Singapore 1992).
- [11] For a careful analysis of the free energy landscape see A. Cavagna, I. Giardinà and G. Parisi, J. Phys. A: Math. Gen. 1997, **30**, 7021 and references therein.

- [12] A. Barrat, R. Burioni, and M. Mézard, J. Phys. A **29**, L81 (1996).
- [13] J.Kurchan and L. Laloux, J. Phys. A **29**, 1929 (1996).
- [14] For review see, W. Gotze, *Liquid, freezing and the Glass transition*, Les Houches (1989), J. P. Hansen, D. Levesque, J. Zinn-Justin editors, North Holland; C.A. Angell, Science, **267**, 1924 (1995)
- [15] J.-P. Bouchaud, L. Cugliandolo, J. Kurchan., M Mézard, Physica A **226**, 243 (1996).
- [16] G. Parisi, in *The Oskar Klein Centenary*, ed. by U. Lindström, World Scientific, (1995), Il nuovo cimento **16**, 939 (1994).
- [17] J.-P. Bouchaud; J. Phys. France **2** 1705, (1992).
- [18] L. C. E. Struik; *Physical aging in amorphous polymers and other materials* (Elsevier, Houston 1978).
- [19] S. Franz and M. Mézard Europhys. Lett. **26**, 209 (1994).
- [20] S. Franz and H. Rieger Phys. J. Stat. Phys. **79** 749 (1995).
- [21] E. Marinari, G. Parisi, F. Ricci-Tersenghi, J.J. Ruiz-Lorenzo *Violation of the Fluctuation Dissipation Theorem in Finite Dimensional Spin Glasses*, cond-mat /9710120.
- [22] B.Bernu, J.-P. Hansen, Y. Hitawari and G. Pastore, Phys. Rev. **A36** 4891 (1987).
- [23] J.-L. Barrat, J.-N. Roux and J.-P. Hansen, Chem. Phys. **149**, 197 (1990).
- [24] J.-P. Hansen and S. Yip, Trans. Theory and Stat. Phys. **24**, 1149 (1995).
- [25] G. Parisi, cond-mat 9701015, J. Phys. A Lett. in press, cond-mat 9701100 J. Phys. A in press, cond-mat 9704046 Phil. Mag. in press.
- [26] G. Parisi, Phys. Rev. Lett. (in press).
- [27] J.-L. Barrat and W. Kob, cond-mat 9704006.
- [28] G. Ruocco, private communication.
- [29] M.Mézard and G.Parisi, J. Phys. A **25** 25 (1996).